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SOME ASPECTS OF SCALING AND UNIVERSALITY IN MAGNETOCALORIC MATERIALS

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ABSTRACT — The magnetocaloric effect of a magnetic material is characterized by two quantities, the isothermal entropy change and the adiabatic temperature change, both of which are functions of temperature and applied magnetic field. We discuss the scaling properties of these quantities close to a second order phase transition within the context of critical scaling theory. In the critical region the isothermal entropy change will exhibit universal scaling exponents. However, this is only true close to T_c and for small fields; we show that for finite fields the scaling exponents in general become field dependent, even at T_c. Furthermore, the scaling exponents at finite fields are not universal: Two models with the same critical exponents can exhibit markedly different scaling behaviour even at relatively low fields. Turning to the adiabatic temperature change, we argue that it is not determined exclusively by the scaling part of the free energy and its derivatives. This means that the field dependence of the adiabatic temperature change in the critical region depends on the regular part (background) of the specific heat associated with the lattice and conduction electrons. The field dependence can still be fitted to a power-law expression but with non-universal exponents as we show explicitly both within mean-field theory and using the so-called Arrott-Noakes equation of state. Finally, we discuss the implications of these observations for the interpretation of a widely used phenomenological scaling procedure.

1. INTRODUCTION

The scaling behavior of the isothermal entropy change and the adiabatic temperature change as a function of applied field is of both technological and scientific interest. From the very discovery of the effect by Weiss and Piccard [1, 2] the field dependence of the magnetocaloric effect has been used to extract information about the intrinsic magnetic properties of ferromagnetic materials, and recently the scaling of both the isothermal entropy change and the adiabatic temperature change has been considered by Franco et al. [3, 4]. The theory of critical phenomena has also been used to justify a widely used phenomenological scaling procedure [5]. However, the applicability of the underlying scaling hypotheses is not self-evident away from the critical region and for finite fields. Here we reconsider these questions based on critical scaling theory and the defining equations for the magnetocaloric quantities. A more extensive discussion of these topics can be found in our recent paper [6].

Critical Scaling Theory

The basic assumption underlying the critical scaling theory of second order phase transitions is that close to the transition temperature, T_c, the free energy (per volume) can be written as a sum of a regular part, F_{reg}, which is analytic at T_c, and a singular part, F_{sing}, which is a generalized homogeneous function (GHF) [7]. This means that there exist scaling exponents a_T and a_H such that for arbitrary positive λ the singular free energy fulfills:

$$F_{sing}(\lambda^{aT}t, \lambda^{aH}H) = \lambda F_{sing}(t,H). \tag{1}$$

Here $t = (T-T_c)/T_c$ is the reduced temperature and H is the applied magnetic field. Physically, the singular part of the free energy is associated with the magnetic degrees of freedom, while the regular part is the background associated with lattice and electronic degrees of freedom. All derivatives of a GHF are themselves GHFs. This means that the magnetization and the singular part of the entropy obey similar relations.

By differentiating (1) with respect to temperature or field it is straightforward to derive the usual scaling forms for the magnetization, $M(t,H) = H^{1/\delta}f_M(tH^{-1/\Delta})$, and the singular part of the entropy, $S_{sing}(t,H) = H^{(1-a)/\Delta}f_S(tH^{-1/\Delta})$, where f_M and f_S are so-called scaling functions. The total entropy is $S(t,H) = S_{sing}(t,H) + S_{reg}(t)$, where the regular part is a function of temperature only. The exponents α, δ and Δ are related to the scaling exponents as follows: $\alpha = 2 - a_T^{-1}$, $\delta = a_H/(1 - a_H)$ and $\Delta = a_H/a_T$. The validity of the scaling relation for, e.g., M implies that if $MH^{-1/\delta}$ is plotted as a function of $tH^{-1/\Delta}$ for different fields, the data will all collapse onto a single curve. However, it is important to note the familiar fact that this collapse will only take place in the critical region close to T_c and even there, the scaling relations will only be valid for small applied fields: Due to the approach of saturation it is unphysical that the relation $M \sim H^{1/\delta}$ should extend to arbitrarily large fields. The size of the critical region depends among other things on the purity of the sample; for single crystal gadolinium, scaling of the susceptibility requires that $|t|$ is less than about $5\cdot10^{-2}$ (corresponding to about 15 K on either side of the critical temperature of Gd, 293 K) and a satisfactory scaling fit of the zero field heat capacity often requires a reduced temperature smaller than 10^{-2} (~ ±3 K around T_c) [8]. These are much narrower intervals than the width of the isothermal entropy change or the adiabatic temperature change at applied fields of the

order of 1 T. The specifics of the deviations from scaling, the so-called corrections to scaling, will not be universal but depend on the details of the materials system, e.g. the precise form of the spin-lattice interaction.

2. SCALING OF THE ISOTHERMAL ENTROPY CHANGE

The isothermal entropy change ΔS is defined as the change in total entropy when the applied field is changed from an initial value (here taken to be 0) to a final value H at a constant temperature T. Since the regular part of the entropy is independent of field, the isothermal entropy change can be calculated from S_{sing} only:

$$\Delta S(t,H) = S_{sing}(t,H) - S_{sing}(t,0). \tag{2}$$

Inserting the scaling relation $S_{sing}(\lambda^{aT}t, \lambda^{aH}H) = \lambda^{1-aT} S_{sing}(t,H)$, which follows from (1), we get that $\Delta S(\lambda^{aT}t, \lambda^{aH}H) = \lambda^{1-aT}(S_{sing}(t,H) - S_{sing}(t,0)) = \lambda^{1-aT}\Delta S(t,H)$. This means that the scaling of ΔS and S_{sing} is the same; consequently we have

$$\Delta S(t,H) = H^{(1-\alpha)/\Delta} f_{\Delta S}(tH^{-1/\Delta}) \tag{3}$$

for some scaling function $f_{\Delta S}$. In particular, at T_c we get a power law dependence of ΔS on applied field with an exponent of $(1-\alpha)/\Delta$. This was previously derived using the scaling of the magnetization together with the Maxwell relation [9].

The fact that the scaling of ΔS is characterized by universal exponents close to T_c is only true for small fields. We have considered the so-called Bean-Rodbell model which is an extension of the ordinary mean field model in which the exchange constant is assumed to depend on the spin-spin distance [10]. This introduces a spin-lattice interaction whose strength is characterized by a dimensionless parameter η; $\eta = 0$ is the ordinary mean field model, while for $\eta < 1$ the model still describes a second-order transition. All models with $\eta < 1$ have the same critical exponents: $\alpha = 0$, $\delta = 3$ and $\Delta = 3/2$. These values imply that the exponent characterizing the field dependence of ΔS is 2/3. However, even though all models belong to the same universality class their scaling exponents at finite fields differ markedly (see Fig. 1), showing that these exponents are not universal [6]. It should be emphasized that the field dependence of the exponents in the Bean-Rodbell model is not a peculiarity of a mean field approach. Rather, it is due to the fact that the phenomenon of saturation is captured correctly in the model.

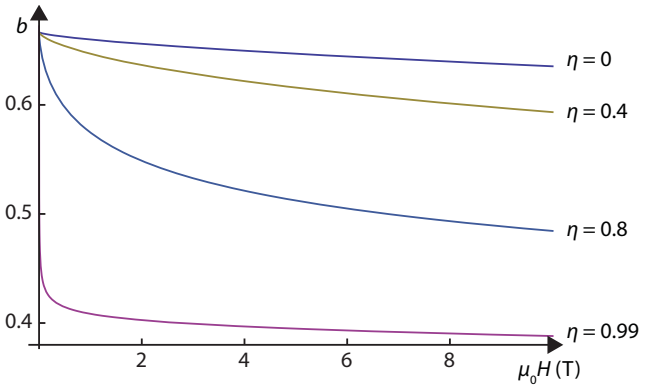

Fig. 1. Scaling exponent b for the isothermal entropy change ΔS for different Bean-Rodbell models. Only for small fields do the exponents approach the value 2/3 predicted from scaling theory. Note that even for $\eta = 0$ there is a (weak) field dependence with b decreasing to 0.64 at a field of 10 T.

3. SCALING OF THE ADIABATIC TEMPERATURE CHANGE

The adiabatic temperature change $\Delta T_{ad}(T,H)$ is defined from the total entropy S through the equation

$$S(T,0) = S(T+\Delta T_{ad},H). \tag{4}$$

Introducing the isothermal entropy change and the total specific heat $C = T(\partial S/\partial T)_H$, (4) becomes the implicit equation

$$\Delta S(T+\Delta T_{ad},H) = -\int_{T}^{T+\Delta T_{ad}} (C(T',0)/T')dT' \tag{5}$$

where the right-hand-side only involves the zero-field specific heat. Incidentally, this form of the equation shows that the adiabatic temperature change can be determined from magnetization measurements (from which ΔS can be calculated) and measurements of C in the temperature region of interest, with no need for low temperature determination of the specific heat. As it stands, (5) is of limited value to discuss the scaling of ΔT_{ad}. This is due to the fact that critical scaling theory only gives the scaling exponents for the singular part of C; its amplitude and the size of the regular background are undetermined in this context, and indeed are not universal. To proceed, we separate the regular part of the specific heat, C_0, from the magnetic part, C_{mag}, and expand (5) to first order in $\Delta T_{ad}/T$ (this requires $\alpha < 0$ [6]) to get

$$\Delta T_{ad} = \frac{-T}{C_{mag}(T,H)+C_0(T)}\Delta S(T,H) + \frac{1}{C_{mag}(T,H)+C_0(T)}(\Delta T_{ad}C_{mag}(T,0) - \int_{T}^{T+\Delta T_{ad}} C_{mag}(T',0)dT'). \tag{6}$$

The scaling behavior of ΔT_{ad} will evidently depend on the relative magnitude of the background specific heat compared to the magnetic specific heat, i.e. it will not be universal. If the last two terms in (6) are ignored, we are simply left with the well-known approximation

$$\Delta T_{ad} = \frac{-T}{C_{mag}(T,H)+C_0(T)}\Delta S(T,H). \tag{7}$$

If either of the two terms in the denominator dominates the other, the result is simple: For $C_0 >> C_{mag}$ the scaling of ΔT_{ad} becomes the same as that of ΔS; in the critical region and for small fields, the field dependence is then characterized by an exponent $(1–\alpha)/\Delta$. For $C_0 << C_{mag}$ the regular part can be ignored and since $C_{mag} \sim H^{-\alpha/\Delta}$ at T_c, the exponent characterizing ΔT_{ad} is $1/\Delta$. The latter result has been derived by Franco et al. [4] who claim that this is a universal result. However, experimentally the two terms are in fact of the same order of magnitude in most (if not all) magnetocaloric materials of interest for near-room temperature applications. This means that neither of the two extreme cases will be relevant, and the field dependence becomes non-universal. If all terms in (6) are kept, the fitted exponent may actually lie slightly outside the interval $[1/\Delta; (1–\alpha)/\Delta]$.

For mean field models $\alpha = 0$, i.e. the adiabatic temperature change will for small fields scale with the same exponent as ΔS. In Fig. 2 we show the scaling exponent for different second order Bean-Rodbell models; the low-field exponent is 2/3 as expected. There is still some field dependence of the scaling exponent but not as pronounced as for ΔS. This means that at finite fields ΔT_{ad} and ΔS scale differently in mean field models with $\eta > 0$, even though $\alpha = 0$.

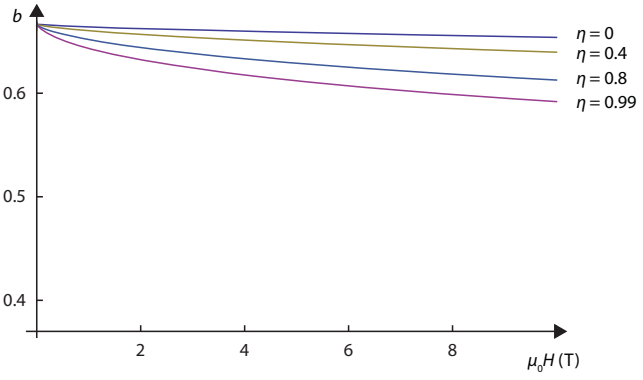

Fig. 2. Scaling exponent b for the adiabatic temperature change ΔT_{ad} for different Bean-Rodbell models.

Going beyond mean field theory, one may consider the so-called Arrott-Noakes equation of state [11]. This has been used extensively in the literature to discuss scaling of the magnetocaloric quantities [3]. The equation of state is of no deep theoretical significance but was originally proposed as a convenient way to summarize the behavior of the magnetization of nickel close to its critical temperature. Exhibiting by construction perfect critical scaling for *all* T, M and H, the equation does not capture the approach to saturation or the low temperature limit correctly. Care should therefore be taken when using the equation to argue for the scaling behavior of the magnetocaloric quantitites. As expected from the perfect scaling behavior, the scaling exponents of ΔS are completely independent of the applied field, which is an unphysical result as we argued above. For the adiabatic temperature change we no longer get perfect scaling for all T and H, even in the Arrott-Noakes equation of state. This is due to the influence of the non-singular specific heat. For concreteness, we have modelled ΔT_{ad} for nickel using slightly modified Arrott-Noakes parameters [11] and the appropriate magnetic [12] and regular [13] zero-field specific heat; for details see ref. [6]. By numerically solving (6) one gets a scaling exponent for ΔT_{ad} as a function of field at T_c of 0.655 at low fields (and only varying about 1% up to 10 T). This is significantly different from $1/\Delta = 0.587$ and very close to $(1–\alpha)/\Delta = 0.645$, in agreement with the fact that C_{mag} is only about 20% of C_0 at T_c. We also see that the exponent in fact lies slightly outside the interval predicted by the approximate expression (7). The fitted exponents have a marked temperature dependence; for $T < T_c$ a simple power law is still a reasonable approximation but the exponent rapidly approaches 1.

The modelling results using the Arrott-Noakes equation can be compared to the experimental results of Weiss and Forrer [14], see Fig. 3. They measured ΔT_{ad} just below T_c; a fit to a power law yields an experimental scaling exponent of 0.79. The modelling results slightly overestimate the data, as should be expected due to experimental heat losses unaccounted for in the present treatment, but the agreement in field dependence (a power law with an exponent of 0.75) is quite satisfactory.

4. PHENOMENOLOGICAL SCALING

A phenomenological scaling procedure for the interpretation of experimental results for the magnetocaloric quantities has been proposed by Franco and coworkers in several papers, see e.g. [3, 5]. It has been justified by the claim that 'states' which have the same value of $\Delta S/\Delta S_{peak}$ (for different fields) are equivalent and therefore should fall on the same 'universal' curve [3]. The scaling is done by taking a set of $\Delta S(T, H_i)$ measurements for different applied fields H_i. For each field the magnitude of ΔS is rescaled such that the peak corresponds to a value of 1, and the temperature axis is rescaled to a θ-axis, such that all curves pass through the points ($\theta = 0$, $\Delta S' = 1$) (corresponding to the peak), $(–1, h)$ and $(1, h)$ where $0 < h < 1$ is in principle chosen arbitrarily.

Apart from the fact that it is slightly misleading to talk about 'states' being associated to quantities such as ΔS and ΔT_{ad} which both are defined from the difference between two *different* thermodynamical states, one can ask whether scaling theory lends support to the phenomenological approach. As noted above, the experimental observation of scaling, even in pure systems, requires rather small reduced temperatures, certainly much less than the 40-100 K or more width of the magnetocaloric quantities in applied fields of 1-10 T. Since $h = 0.5$ is often chosen for the rescaling, even the interval $-1 < \theta < 1$ goes far beyond the critical region. For impure systems, the critical region is smeared out, making observation of criticality even more difficult. These arguments show that critical scaling cannot be invoked as the reason for the success of the phenomenological approach. In any case, the highly constrained nature of the rescaled curves for $-1 < \theta < 1$, where all curves pass through the same three points, ma-kes the phenomenological scaling procedure of limited value to detect the presence or absence of critical scaling. Indeed, both Bean-Rodbell models with $\eta = 0$ and with $\eta = 0.8$ show perfect collapse for a field range of 0-2 T, even though the $\eta = 0.8$ case is very far from exhibiting universal scaling due to the large field dependence of the exponents (cf. Fig. 1) [6]. It is also noteworthy that both theoretically and experimentally there seems to be no clear connection between the absence or presence of phenomenological collapse and the order of the phase transition [6, 15].

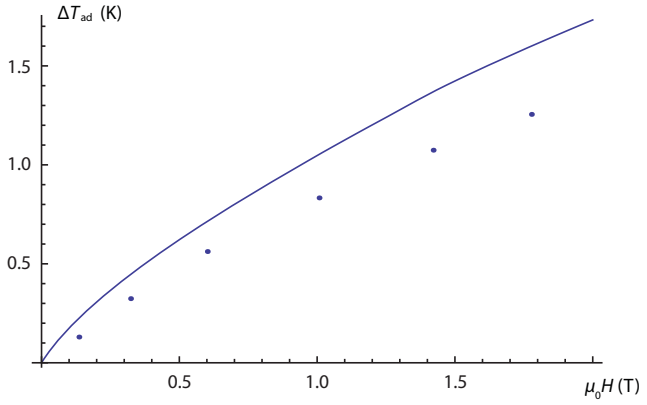

Fig. 3. The adiabatic temperature change of nickel measured at 356.24 °C, just below $T_c = 357.6$ °C, as determined by P. Weiss and R. Forrer [14]. The full line is calculated from (6) using the Arrott-Noakes equation of state.

5. CONCLUSION

We have discussed the scaling of the magnetocaloric quantities within the context of the theory of critical phenomena. For the isothermal entropy change the field dependence close to T_c and for small fields is characterized by a universal exponent; this is not true for the adiabatic temperature change whose scaling also depends on the size of the regular background specific heat. At finite fields, the exponents associated with ΔS become non-universal. We also argue that a widely used phenomenological scaling procedure for the magnetocaloric quantities cannot be theoretically justified by an appeal to scaling theory.

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